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<p><b>(54) Title:</b> FIRE RETARDANTS AND PRODUCTS PRODUCED THEREWITH</p> <p><b>(57) Abstract</b></p> <p>Improved fire retardant compositions, methods of making such compositions, and wood and other cellulosic products treated with such compositions which comprise a major amount of boric acid and a minor amount of (a) one or more synergist materials which, with boric acid, enhance the fire retardant properties of treated products as compared to boric acid or the synergist alone, and (b) optionally, one or more solubilizers which increase the water solubility of boric acid. The compositions are of substantially neutral pH and do not cause metal corrosion or acid hydrolysis of treated products.</p>			

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FIRE RETARDANTS AND PRODUCTS PRODUCED THEREWITH  
RELATED APPLICATION

BACKGROUND OF THE INVENTION

Many different compositions have long been used in treatment of wood and other cellulosic materials to provide a degree of fire retardant properties to such materials. Such properties most commonly have been obtained (1) by depositing on the surface of an article (either an article of manufacture or cellulosic particles from which a manufactured article is to be formed) a coating comprising either (a) a composition containing a finely divided solid material having fire retardant properties, or (b) an intumescence composition which, on exposure to the high temperatures of burning, decomposes pyrolytically to form a protective, insulating char layer on the coated article, or (2) by impregnating such materials with a fluid composition capable of penetrating the interstices of solid wood or other cellulosic material to be treated and which composition, and/or one or more decomposition products thereof which, on exposure to wood pyrolysis temperatures, reacts with wood before pyrolysis to form, primarily, carbon and water (in the form of steam).

Typical of surface coating type composition are those comprising fire retardant solid materials in precipitated or otherwise finely divided form, such as: silica; carbonates and bicarbonates of sodium, potassium or ammonium; diammonium phosphate, or particulate metallic elements such as aluminum (Stossel U.S. Patent No. 4,076,540 which also provides an extensive description of prior art fire retardants). Such materials may be applied, in the form of solid powders, or pastes or suspensions to the surfaces of wood articles to be treated, for example as shown in Handa et al. U.S. Patent No. 3,811,992. Such prior art compositions suitable for the limited purpose of surface treatment of fibrous cellulosic materials or of wood particles for the manufacture of

fiberboard and similar materials also include ionic complexes of nitrogen, phosphorus, oxygen and aluminum together with a boric acid compound and urea (Stossel U.S. Patent 4,076,540); and suspensions of boric acid with water-soluble borate salts such as those of ammonia, alkali metals and alkaline earth metals, for example borax (sodium tetraborate,  $Na_2B_4O_7 \cdot 10H_2O$ ) (Dietrich et al. U.S. Patent No. 4,801,404). Also in this category of fire retardant compositions is Schaar et al. U. S. Patent No. 3,955,987 which is directed to a temporary intumescent coating in either dry powder form or in the form of an aqueous suspension containing monoammonium phosphate and/or diammonium phosphate as a fireproofing agent, urea and/or dicyandiamide (cyanoguanidine) as a gas forming agent to promote intumescence, a polyol such as mono-, di- or tripentaerythritol, starch, or sugars such as inositol, dextrose or sucrose as promoters of initial, low temperature intumescence, and titanium dioxide as a heat-reflecting agent. By reason of the solid physical state of such compositions or components thereof, they cannot be impregnated into solid wood and hence are useful only for surface treatment of wood articles or of particles of wood and other cellulosic materials used in the manufacture of other articles. All coatings are designed to form insulating barriers and do not promote catalytic dehydration of the wood substance.

Surface coating fire retardants may be in the form of a resin and also may contain a boron compound. Such compositions include, for example, those containing a phosphoric acid-dicyandiamide-formaldehyde resin, such as disclosed in Surdyk U. S. Patent No. 3,874,990, wherein the resin component is used together with an alkaline borate such as a mixture of borax and boric acid (or sodium polyborate) and a binding resin such as a urea- or melamine-formaldehyde resin. Other examples include: boric acid ester resins impregnated into particle board and then hydrolyzed to deposit boric acid or boron oxide within the wood product (Short et al. U. S. Patent No. 4,076,871); urea-formaldehyde and boric acid or sodium phosphate, ammonium bromide, or an ammonium salt such as the phosphate, sulfate, or sulfamate; urea, borax, a

polyvinyl alcohol and a polyhydric alcohol; urea and one or more of boric acid, borax and ammonium phosphate; boric acid and urea, thiourea or dicyandiamide; urea-formaldehyde resin and borax; polyvinyl chloride or polyethylene with borates or boron oxide; and the above-described ionic complex-boric acid-urea compositions (containing at least 23% urea) which also can be applied in aqueous resin form (for a more detailed description of such compositions see Stossel U.S. Patent No. 4,076,540); polymers such as melamine, dicyandiamide, anhydrous borax, borax decahydrate (or boric acid), ammonium polyphosphate and monoammonium phosphate -- for addition to a plastic material during manufacture thereof (Schmittmann et al. U. S. Patent No. 4,438,028); Junega U. S. Patent No. 3,832,316 and Junega Canadian Patent No. 917,334, directed to fire retardants containing dicyandiamide, melamine, formaldehyde and phosphoric acid wherein a minor portion of the phosphoric acid may be substituted with another acid, such as boric acid; and Handa et al. U. S. Patent No. 3,811,992 which discloses pretreating plywood with a silicate material such as sodium silicate or alkoxy silanol polymers with a deliquescent material such as ammonium bromide (which inhibits the low temperature flashing tendency of the silicon compounds), then coating the pretreated plywood with a fire retardant in the form of an aqueous paste comprising 20-35% of a urea compound such as thiourea, dimethyl thiourea or monomethylolmelamine, and 10-20% of an ammonium halide with optional amounts of an organo-phosphorus or organo sulfur compound generating a fire retarding vapor at a pyrolysis temperature over about 400 deg. C, for example tricresyl phosphate, glycerine phosphate, guanidine phosphate or ammonium sulfamate, a metal halide such as zinc chloride, a sulfate such as ammonium sulfate, and a weak acid such as boric acid or a weak acid compound such as ammonium borate or ammonium phosphate, an antimony compound such as antimony trioxide or antimony trichloride, a sulfoxide and formaldehyde.

When used as surface coatings, resinous and paste-like materials, alone or together with other composition components, serve the fire retardant function by forming, on the surface

of the treated wood article or wood particles from which an article is to be formed, an insulating carbonized coating, which, in some cases, may be foamed to increase the insulation properties. Upon subjecting large areas of such coated materials to carbonizing temperatures (such that the heat energy is not conducted away), the untreated wood under the coating pyrolyzes, cracks form in the coating from which volatilized gases issue and burn. Under prolonged exposure to such conditions, the entire mass of the wood may be consumed.

Superior resistance to burning of wood products is obtained by impregnating the wood mass with a fire retardant material. However, it is difficult or impossible to impregnate dense solid wood with fire retardant compositions in viscous resinous form. Some such compositions, having a sufficiently low viscosity, lend themselves to at least a limited degree of permeation into relatively porous wood, particle board and similar porous cellulosic products. Even in such cases, impregnation and curing of the resin ordinarily is very time consuming and requires extended times at high temperatures, e.g. upwardly of 180°F - 300°F, which can impair wood strength properties. For example, the above-mentioned Handa et al. U.S. Patent No. 3,811,992 shows the need for a 15 hour period for permeating a 4 mm thick wood panel at ambient temperature, followed by an elevated temperature treatment in an electric drier. The above-described Short et al. U. S. Patent No. 4,076,871, discloses, as a necessary step for treating 1/4 inch thick hardboard panels, kiln heating panels coated with the borate-containing resin for 1-1/2 to 2 hours at 150°C to 165°C (302°F to 329°F) in order to cause the resin to penetrate into the board.

Prior art fire retardants suitable for impregnation of solid wood articles include, for example: Goldstein U. S. Patent No. 2,917,408 directed to a composition containing dicyandiamide and phosphoric acid; Goldstein U. S. Patent No. 3,159,503 wherein such a composition additionally contains a small amount of formaldehyde, and Steez U. S. Patent No. 4,174,223 which discloses a water-soluble composition comprising ammonium nitrate, ammonium polyphosphate, urea (over

30 weight percent) and, optionally, a base such as sodium hydroxide, and molasses, sugar or starch to aid in the retardation of flaming and afterglow. Such compositions which also contain boron are exemplified by: Lewchalermwong U. S. Patent No. 4,725,382 wherein the fire retardant composition contains boric acid (in the form of the anhydrides,  $B_2O_3$ ), phosphorus pentoxide and ammonia; and Goettsche et al. U. S. Patent No. 4,461,721 which provides a wood preservative (and flame-proofing) composition containing a boric acid salt of a water-soluble amine such as monoethanolamine, water and sodium polyborate (or a mixture of boric acid and borax).

In addition to fire retardant action per se, fire retardant compositions must possess other important properties for their general acceptability and application. For example, acceptable fire retardants must not release or promote production of dangerous amounts of poisonous gases or fumes on burning. As exemplified in several of the above-described patents (for example, Surdyk U.S. Patent No. 3,874,990), many prior art fire retardants, especially those having a resin as the effective ingredient, contain formaldehyde or other material forming formaldehyde as a high temperature reaction product. Formaldehyde is considered a carcinogen, and products containing or releasing substantial amounts of formaldehyde during processing or on exposure to high, pre-pyrolysis temperatures pose significant health hazards.

Compositions comprising, as the effective fire retardant, compounds having a high degree of ambient temperature solubility in water are quickly leached out of impregnated wood products on exposure to weathering conditions, so are not suitable for treating wood articles intended for prolonged exterior and underground construction applications. Examples of water-soluble materials which have been used in fire retardant compositions include phosphoric acid, ammonium salts such as ammonium phosphates, ammonium chloride or ammonium sulfate, and soluble metal salts such as chlorides of zinc, sodium or magnesium. (See, for example, Handa et al. U.S. Patent No. 3,811,992 -- metal halides such as zinc chloride, also alkali metal silicates such as sodium silicate;

Schmittmann U.S. Patent No. 4,438,028 -- borax; Gottsche et al. U.S. Patent No. 4,461,721 -- sodium tetraborate; Dietrich U.S. Patent No. 4,801,404 -- alkali metal and alkaline earth metal salts). Metal-containing compositions, especially those containing alkali metals and alkaline earth metals (e.g. as disclosed in the Dietrich patent and in Surdyk U.S. Patent No. 3,874,990), are glowing accelerators, that is, they promote wood combustion by glowing, and accordingly, compositions containing substantial amounts of such materials are undesirable components of fire retardant compositions. Such fire retardant materials have the further objectionable features of causing smoky burning and possible production of toxic fumes. Such objectionable results also are produced on combustion of wood treated with fire retardants containing bromine, for example, as in the compositions disclosed in the Handa U.S. Patent No. 3,811,992. Another serious shortcoming of many prior art fire retardant compositions is their high degree of hygroscopicity. In general, in drying prior art fire retardant-treated wood products, the moisture content is reduced to under about 10% of the product weight. The composition of the treated product should be such that it does not absorb further substantial amounts of water in excess of that which would exceed the fiber saturation of the wood product itself. Accordingly, fire-retardant compositions should be free of hygroscopic ingredients which would cause such excessive water absorption.

It is known to the prior art that fire retardant compositions should be essentially non-hygroscopic or of low hygroscopicity, in order to avoid undue moisture absorption by treated wood products. For example, Oberley U. S. Patent No. 4,373,010 teaches that use of hygroscopic materials as fire retardants or as components of such compositions should be avoided to prevent blooming of the wood. Blooming results from water absorption by wood to an extent to form liquids allowing salts to migrate to and deposit salt crystals on the wood surface. This interferes with or prevents painting or other surface treatment of the wood product. High water content of treated products containing water-soluble acids or acid-forming

compounds also provides the conditions for corrosive attack of metals in contact with such products and, as discussed in more detail below, for acid hydrolysis of the wood cellulose.

Hygroscopic materials may be present as original components of the fire retardant or they may be formed as reaction products during preparation of the fire retardant composition, for example, on heating of the composition to solubilize the fire retardant component, or during drying of the treated wood products at elevated temperatures.

Fire retardant compositions comprising or containing substantial amounts of such hygroscopic materials are not generally useful and are to be avoided in many or most permanent wood-treating applications.

Hygroscopic materials which have been used in fire retardants prominently include, for example: urea -- which is very hygroscopic (for example, the Oberley U.S. Patent No. 4,373,010 mentions that urea should be held under about 15% in order to avoid its strong hygroscopic action); alkali metal salts such as sodium chloride, sodium sulfate; other metal salts such as magnesium chloride, and ammonium sulfamate. Examples of prior art fire retardant compositions comprising such hygroscopic materials include those described in: Handa et al. U. S. Patent No. 3,811,992 (except as hygroscopicity is reduced by adding formaldehyde); Surdyk U. S. Patent No. 874,990; Schaar et al. U. S. Patent No. 3,955,987; Stossel U.S. Patent No. 4,076,540; and Schmittmann U. S. Patent No. 4,438,028.

As illustrated by certain of the above described prior art patents, phosphoric acid and its salts, such as ammonium phosphates, are very common constituents of prior art fire retardants. The term "phosphoric acid" refers to orthophosphoric acid,  $H_3PO_4$  and corresponding hydrated compounds such as  $2H_3PO_4 \cdot H_2O$ , which is the oxy acid of phosphorus most commonly available and used, and to which reference usually is made when such term is used; although the term phosphoric acid also may be used to include any or all of the other oxy acids of phosphorus such as:  $H_3PO_3$  (phosphorous acid);  $H_4P_2O_7$  (pyrophosphoric acid);  $H_4P_2O_5$  (pyrophosphorous

acid);  $H_3PO_2$  (hypophosphoric acid),  $H_4P_2O_6$  and  $HPO_3$  (metaphosphoric acids), the polyphosphoric acids and mixtures of the above. Orthophosphoric acid,  $H_3PO_4$ , is a tribasic acid, having a  $pK_1$  of about 2 in aqueous solution; accordingly, it is a strong acid. As is well known, the term  $pK$  refers to the negative logarithm of the dissociation constant,  $K$ , of a particular chemical compound to which reference is made.  $pK_A$  and  $pK_B$  conveniently are used, respectively, as measures of acid or base strength. Acid or base strength decreases as  $pK_A$  or  $pK_B$  increases.

A strong acid, such as phosphoric acid, is a desirable ingredient of fire retardant compositions in order to react with wood at or below pyrolysis temperatures to form reaction products such as water, ammonia and non-combustible carbon -- rather than combustible carbon containing tar and gases which result in heat generation and flame spread. However, phosphoric acid per se, is not a good fire retardant because it forms pyrophosphates at combustion temperatures and such compounds have no significant fire retardant action in accordance with usual test standards. Moreover, use of the highly acidic phosphoric acid per se would pose a manufacturing and handling safety hazard. The alkali metal phosphates and alkaline earth metal phosphates are not effective fire retardants because (in addition to the above-described afterglow effect which they promote) they retain a substantially neutral pH on heating and cannot serve as catalytic dehydrating agents to form carbon and water -- a common theory of this mode of fire retardancy. On the other hand, ammonium phosphates are acidic and have good fire retardance properties. Polyphosphates, of high acidity and good fire retardance, are formed under the high energy conditions prevailing at combustion temperatures. However, these desirable properties tend to be lost and the less fire retardant pyrophosphates tend to be formed under these conditions. Ammonium phosphates release ammonia which reduces the rate of formation of the non-fire retardant pyrophosphates and thereby increases the time during which the desirable fire retardance properties of polyphosphates can be exerted.

The value of using, as components of fire retardant compositions, a material such as phosphoric acid, which, under ambient conditions, exhibits high acidity, unfortunately has still other accompanying serious disadvantages. For example, it long has been known that fire-retardant compositions of high acidity and hygroscopicity are corrosive to metals in contact with the treated wood products. In general, the more acidic the fire retardant composition, the greater is the corrosion problem. Acidic anions used in fire retardant compositions generally are selected from the following group: halide, e.g. bromide or chloride; sulfate; nitrate; phosphate, and borate -- in descending order of acidity. Strongly acidic and hygroscopic compositions have the further disadvantage of seriously affecting the strength properties of wood products due to acid hydrolysis of the wood cellulose in prolonged contact with such fire retardant compositions. This effect only recently has been recognized and treated as a serious problem by regulatory agencies, the construction industry, and the insurance business. As a result, the use of fire retardant compositions causing dangerous strength loss due to their strongly acidic nature has been restricted or banned in several states.

Examples of highly acidic prior art fire retardant compositions include those disclosed in Handa et al. U.S. Patent No. 3,811,992; Schaar U.S. Patent No. 3,955,987; Stossel U.S. Patent No. 4,076,540, and Steez U.S. Patent No. 4,174,223. The compositions of U.S. Patent 4,373,010, sold by Hickson Ltd. under the trademark "DRICON," comprise aqueous solutions of fire retardant compositions with which solid wood is easily impregnated and containing, by weight of the composition prior to reaction, from 60 to 90% (preferably about 70%) of dicyandiamide plus phosphoric acid -- which are reacted to form guanylurea phosphate ("GUP") -- and from 10 to 40% (preferably about 30%) of boric acid. This combination of ingredients acts synergistically, the reaction product, "DPB," exhibiting a greater reduction of fire weight loss as compared to the individual components of the mixture. Such compositions are believed to be the only commercially produced fire retardant

products for pressure treating of wood which currently are allowed unrestricted marketing in all states of the United States. This is due in part to the lesser degradation of wood by acid hydrolysis than other prior art commercially available fire retardants. However, such compositions contain reaction products, such as guanylurea phosphate, which are highly acidic under high ambient temperature and humidity conditions and therefore result in at least a moderate degree of acid hydrolysis and corresponding wood strength loss during kiln drying and/or with prolonged exposure to high moisture conditions. Consequently, there is a compelling need for fire retardant compositions which do not have the serious shortcomings of those based upon a phosphoric acid-ammonium phosphate system.

Due to the very low acidity of boric acid, its use in a fire retardant composition would be preferable to stronger acids such as phosphoric acid, especially under hygroscopic conditions, in order to reduce metal contact corrosion and the wood-degrading effects of acid hydrolysis. However, as also described in U.S. Patent No. 4,373,010, boric acid alone has little fire retardant effect over a wide range of boric acid impregnant, for example, over a range from 0.5% to 2.5% boron retained in wood, for example as resulting from treatment under atmospheric pressure with an aqueous solution containing 10% by weight of boric acid.

Effectiveness of a fire retardant composition is increased, up to a point of maximum effectiveness (the "threshold value"), with increasing amount of the composition which is impregnated into a treated wood article. Therefore, it is desirable to be able to provide high concentrations of the effective fire retardant materials in aqueous solutions for treating wood products, especially high density woods. However, in view of the limited low (e.g. ambient) temperature solubilities of many such materials, such as boric acid, it is difficult or impossible to attain a desired or effective level of retained fire retardant during impregnation of wood products. Such problems were partially overcome in the compositions of Oberley U.S. Patent No. 4,373,010 wherein the

low temperature solubilities of both boric acid and GUP are increased substantially when those materials are present together in a water solution. For example, in a 25°C water solution, solubility of a 70% GUP-30% boric acid mixture is 18%, compared to solubilities of 9% for GUP and 5% for boric acid in separate water solutions at the same temperature. That patent also shows that guanylurea phosphate (GUP) has somewhat better fire retardant properties at higher boric acid concentrations (e.g. over about 1.24% retained boron content in treated wood), and that the reaction product formed in preparation of GUP/boric acid compositions has a synergistic effect on fire weight loss.

Thus, in accordance with the above-described prior art, the use of boric acid as the sole or major component of fire retardant compositions, for example, in place of phosphoric acid, would be considered ineffective due to its low acidity and fire retardancy, as well as its limited low temperature solubility -- even as those properties are enhanced by the phosphorus-based compositions of Oberley U.S. Patent No. 4,373,010.

#### SUMMARY OF THE INVENTION

The objects of this invention include the provision of improved boric acid fire retardant compositions, methods for making the same, and wood and other cellulosic products treated with such compositions. When such compositions are incorporated in water solution, a major portion of the solute phase comprises boric acid and a minor portion comprises materials increasing the water solubility of boric acid and its fire retardancy. Such compositions are essentially free of or contain only controlled, low amounts of strong mineral acids or acid salts, are substantially non-hygroscopic or of controlled, low hygroscopicity. Solid wood and other cellulosic products impregnated with such compositions are essentially non-corrosive to juxtaposed metals and the strength properties of the impregnated products are substantially unaffected by acid hydrolysis.

## DETAILED DESCRIPTION OF THE INVENTION

Contrary to the teachings of the prior art, as above described, I now have found that there can be produced a composition for treating wood and other cellulosic products -- for example, but without limitation thereto, paper, cardboard, cotton, jute and hemp -- (such cellulosic products generally being referred to herein as wood or wood products), and comprising an aqueous solution, produced at ambient or only slightly elevated temperatures, in which the solute (that is, the charged materials, excluding water) contains boric acid in amounts upwardly of 40%, preferably at least 45%, and especially at least 50%, by weight of the solute, together with minor proportions of boric acid solubilizers and certain water soluble, nitrogen-containing synergists which enhance effectiveness as a fire retardant. In addition to excellent fire retardancy, such compositions also have low metal corrosivity and are without significant hydrolytic degradation of the treated wood products.

The term "boric acid" commonly is used in reference to one or another of several compounds which differ from one another by the amount of chemical water content of the compounds. Representative compounds include  $B(OH)_3$  (boric acid),  $HBO_2$  (metaboric acid),  $H_2B_4O_7$  (tetraboric acid),  $B_2O_3$  (boric oxide or boric anhydride) and mixtures thereof, and it is to be understood that such compounds may be referred to herein as boric acid unless otherwise indicated in a particular context.  $B(OH)_3$ , the compound most generally referred to by the term boric acid, is a very weak monobasic acid which tends to form polymeric structures in mixed solutions with borates. As above indicated, boric acid solubility in cold water ( $20^\circ C$ ) is about 5 parts per 100, increasing to about 40 parts/100 at  $100^\circ C$ . Boric oxide,  $B_2O_3$ , is slightly less soluble (about 1.1 part per 100 in water solution at  $0^\circ C$  and about 16 parts/100 at  $100^\circ C$ ) and, with water, forms  $B(OH)_3$ .

The comparatively low ambient temperature water solubility of boric acid is of advantage in boric acid-based fire retardants in that wood treated with such compositions can be used for certain outdoor applications, such as temporary

construction, while retaining fire retardancy longer than compositions containing more soluble ingredients as above described.

As previously described, boric acid is the least acidic of the acid anions commonly found in fire retardant compositions, being of nearly neutral pH in aqueous solution at ambient temperatures. The basic equilibrium constant,  $pK_A$ , for boric acid,  $B(OH)_3$ , is in the range of about 7 to about 9 depending upon the particular structure and molar concentration in water solution. Thus boric acid is a very "weak" acid as compared, for example to phosphoric acid and the other "strong" mineral acids above-described as commonly used in prior art fire retardant compositions.

It is believed that the relative ineffectiveness of boric acid alone as a fire retardant is due to the formation of boron oxide,  $B_2O_3$ , which is non-fire retardant -- but is a strong glow inhibitor. Although a fire retardant composition based on ammonium phosphate is a good fire retardant because of the slow loss of ammonia, a combination of boric acid and ammonia is not. At elevated temperatures, e.g. above about  $250^{\circ}C$ - $300^{\circ}C$ ., at which wood begins to pyrolyze at a rapid rate, acidity of boric acid increases, approaching that of phosphoric acid, so that it can react with ammonia to produce transient acidic ammonium salts, such as ammonium tetraborates, which, as fire retardants, are about as effective as are ammonium phosphates. However, these reaction products are thermally unstable even at high ambient temperatures, and at more elevated temperatures substantially all of the ammonia in an impregnated wood product is lost quickly by volatilization, leaving boric acid which, at wood pyrolysis temperatures, forms the non-fire retardant  $B_2O_3$ . However, I have discovered that a superior fire retardant composition can be made by providing, in combination with boric acid and water, a material which substantially increases the low temperature water solubility of boric acid in aqueous solution, and a non-acidic nitrogen-containing material which is not subject to the above-described shortcomings of an ammonia-boric acid system and which, with boric acid, provides a synergistic effect in

enhancing fire retardancy of wood products treated with such compositions.

Useful nitrogen-containing synergists include such water soluble, nitrogen-containing compounds as semicarbazide, guanidine, cyanamide, dicyandiamide, urea and guanylurea. Melamine, biuret and oxamide also are useful synergists, but they have low water solubility at the comparatively low temperatures normally used for production of the compositions of this invention. If such materials are used as the sole synergist(s), their solubility can be increased by use of an appropriate additional solubilizing agent. For example, solubilization of one mol of melamine can be obtained with use of about 1/2 mol of formaldehyde. For my purposes, these synergist materials are not adequate solvents for boric acid, but in combination with boric acid they provide excellent improvement in fire retardancy as compared to such materials or boric acid alone.

I believe that the synergistic action of these nitrogen-containing materials is due mainly to the protection which they afford against the formation of non-fire retardant boron oxide during heating and burning of wood treated with such compositions. At wood combustion temperatures, the nitrogen-containing synergists decompose, providing a continuous supply of ammonia which, together with successively-produced intermediate reaction products, react with the now acidic boric acid, forming highly acidic borates and adducts and with the production of steam (along with carbon from the wood cellulose). The involved catalytic dehydration reactions retard the ultimate formation of non-fire retardant  $B_2O_3$  (and pyrophosphates, if the composition contains phosphorus compounds) for a time sufficient to allow the suppression of combustion. In accordance with this understanding, there may be considered, for example, a composition containing, dicyandiamide ("dicy") as the synergist. At pyrolysis temperatures, the "dicy" hydrolyzes to guanylurea; the guanylurea reacts with boric acid to form the corresponding acidic borate; the borate is hydrolyzed to guanidine borate and ammonia; the guanidine borate is further hydrolyzed to

urea-boric acid adduct and additional ammonia; the adduct further hydrolyzes to transient ammonium borate which ultimately leads to the formation of boron oxide.

Such systems therefore provide fire retardant compositions which are essentially non-acidic at room temperature -- hence they do not result in acid hydrolysis of impregnated wood -- but, on heating to wood combustion temperatures, they become strongly acidic and hence are good fire retardants.

Effective solubilizing agents for the boric acid include strongly basic non-alkali metal, non-alkaline earth metal nitrogen-containing compounds, for example, those having a pK value under about 5, preferably under 4, (the  $\text{PK}_B$  value for ammonia in aqueous solution at  $25^\circ\text{C}$  is 4.75) such as: ammonia; basic amines, including primary, secondary and tertiary alkylamines and alkanolamines (amino alcohols) such as mono-, di- and triethylamines; mono-, di- and tripropylamines; mono-, di- and triethanolamines, and mono-, di- and tripropano- lamines, and addition compounds such as hexamethylenetetramine and those formed by reaction of formaldehyde (for example, when used as a solubilizer for certain synergists, as aforesaid) and amines such as urea or melamine, or dicyandiamide used as synergists. Suitable boric acid solubilizers also include substantially pH-neutral or weakly basic nitrogen-containing compounds (pK of about 5 or greater), for example: hydrazine; hydroxylamine, ammonium carbonates and ammonium carbamate. Another type of suitable solubilizer includes alcohols such as the lower (water soluble) saturated monohydric alcohols such as methanol, ethanol, n-propanol, isopropanol, and butyl and amyl alcohols; and polyols, including dihydric alcohols such as ethylene glycol and propylene glycol, trihydric alcohols such as glycerol (glycerine), higher polyhydric alcohols, for example, mannitol and sorbitol, and the monosaccharides and disaccharides. Preferred monohydric alcohols are methanol and ethanol, especially methanol. In the polyhydric alcohol category, glycerol is preferred. In the category of sugars, sucrose is preferred. Although, in dilute solutions, sugars are readily

impregnated into wood products, when the products are dried, they tend to have a somewhat sticky surface. Therefore such solubilizers are not preferred for some applications.

Solubilization of boric acid is promoted by its reaction with the lower alcohols and polyhydroxy compounds such as the trihydric alcohol, glycerol, and the monosaccharides and disaccharides, alone or mixed with ammonia, to form equilibrium borate esters and complexes which effectively increase the rate and extent of solution of boric acid.

In the case of solubilizers which can react to form resinous materials, for example borate esters or formaldehyde reaction products, such solubilizers required for effective boric acid solubilization are limited to an amount sufficiently small as to avoid the formation of such quantities of viscous resinous materials as would interfere with the impregnation of wood products or give rise to the need for high temperature curing of the treated products. Unlike the ammonia-boric acid system, the compounds formed as reaction products of boric acid with the contemplated boric acid solubilizers do not completely volatilize or precipitate under ambient conditions. After drying of wood products impregnated with such compositions, some of these reaction products remain in the wood.

Some of the contemplated nitrogen-containing solubilizers, for example, the alkylamines, also may serve a synergistic function in the compositions of this invention. Such action depends upon the particular organic radical and the nature of the chemical bond involved. Depending upon such factors, as well as the decomposition rate and the combustible carbon content of such materials, such materials may tend to promote flame spreading upon exposure to burning temperatures. In general, the larger the organic radical, the more fuel it adds and the more combustible it is. However, the latter characteristic is not contraindicative of use of such materials in my fire retardant compositions, where, for example, the amount required for solubilization is relatively small and the synergistic effect is pronounced. In such cases,

the advantages gained in boric acid solubilization and synergistic effect on fire retardance may outweigh the flame spreading potential of such materials.

Mono- and diammonium phosphates and guanylurea phosphate also are useful as boric acid solubilizers, and these materials also have the desirable characteristic of acting, with boric acid, as synergists in effect on fire retardancy. Phosphoric acid, in limited amounts, also can serve a role as a supplemental fire retardant in the compositions of the invention. However, in view of the strongly acid nature of such materials, they must be used in small quantities or they will cause unacceptable acid hydrolysis and corresponding strength loss of treated wood products. Thus, such materials are limited in combined amount to less than about 20%, preferably less than 15 or 16% by weight of the solute (charge materials, excluding water).

When phosphorus compounds are added to the formulation, the boric acid content can be reduced by an amount about equal to the phosphoric acid equivalent in the phosphorus compound. The compositions of the invention are most effective when the molar ratio of N to B or B+P is from about 0.5:1 to about 2:1, preferably about 0.8:1 to 1.5:1, depending on the degree of synergism of the nitrogen-containing synergist compound.

The compositions of the invention can be prepared in the form of a dry powder mixture of those components which are of solid form at ambient temperatures. If ammonia is included in the composition, the dry formulation may include ammonium carbonate. Other components, in liquid form at ambient temperature, may be added when forming an aqueous fire retardant solution. Aqueous solutions, containing the contemplated solubilizers and combined solubilizer/synergists, can be prepared at fairly low temperatures and containing larger amounts of boric acid than heretofore have been employed. Thus, it is possible to prepare such solutions containing boric acid in amounts upwardly of 5% to about 15 or 20% by weight of the solution and wherein the boric acid comprises over 40 to 45% to about 70% by weight of the charge materials. The capacity of woods to absorb water and such

treating solutions varies greatly, for example by increasing wood weight from under 100% to over 200%. Thus, the concentration of boric acid in the treating solutions of this invention correspondingly may vary over a wide range. In such context, solutions for use directly in treating most wood products, for example those capable of about 150% weight increase on treatment, may contain boric acid in amount from about 5 to about 9 or 10 weight percent of the solution and wherein the boric acid comprises, by weight percent of the charge materials, from about 45%, especially at least 50%, to about 65%, and particularly about 60%.

Preparation of aqueous solutions of the contemplated fire retardant compositions can be carried out by adding the component chemicals to water at a temperature from close to 0°C, especially about 20°C., to about 100°C. At the lower end of this range, solution of boric acid may require use of solubilizers of greater solubilization capacity and/or in greater amounts than required at higher temperatures. The higher end of such range is not necessary and is not preferred in preparation of compositions containing materials, such as ammonia, having high rates of volatilization at such elevated temperatures. A practical processing temperature range between about 30°C. and 60°C., especially about 30°C. to about 45°C., is preferred. A preferred method is to add the boric acid and solubilizer(s) to water and agitate the mixture until the boric acid is dissolved, and then add the synergist(s) followed by any remaining water and other ingredients, and then allowing the solution to cool to ambient temperature. In an alternate method all of the chemicals can be added, for example, to about 20°C to 45°C water, and agitated until the chemicals are dissolved. Such aqueous solutions may be prepared with solute contents suitable for use directly as wood treating compositions, or they may be prepared in the form of more concentrated solutions which may be diluted with further amounts of water, as desired.

The factor ultimately determining the amount of solubilizer to be used in making a fire retardant treating solution in accordance with this invention is the amount of

boric acid (and synergist) to be introduced into a particular wood product to be treated. This depends upon the degree of fire retardance desired for the wood product and the solution absorption capability of the wood product at a particular treating temperature. Once such factors are known, the required amount of solubilizer can be determined in terms of the corresponding required concentration of boric acid in the treating solution and, in turn, the solubilization capacity of a particular selected solubilizer and the temperature to be used in making the fire retardant treating solution. Factors affecting solubilization capacity, hence selection and amount of a particular solubilizer, include, for example, its basicity and rate and extent of reaction with boric acid and with other ingredients of the composition, for example by formation of addition compounds, borate esters or complexes, or the ability to increase the acid strength and availability of boric acid for reaction. Other known chemical and physical characteristics of the solubilizer, such as volatility, ignition temperature, and flame spreading or inhibiting tendency, also are to be considered in selecting and determining the amount of particular solubilizers.

A practical advantage of the preferred, solubilizer-containing compositions of this invention and the method of preparing aqueous solutions of those compositions is that the solutions can be made at the above-described preferred, comparatively low temperatures in the range of about 20°C. or 30°C. to about 45°C. Such processing requires less energy than do temperatures in the higher portion of the broad temperature range, and at the lower temperatures there is less loss of any volatile process materials. Moreover, such solutions can be stored and handled at ambient temperatures without precipitation of solute components. Storage of aqueous solutions of the compositions of the invention normally is at temperatures well above freezing, in order to avoid precipitation of dissolved compounds. However, these compositions have the further advantage that, if frozen, they can be reheated and the solute redissolved without reducing the effective fire retardancy of the compositions. Nevertheless,

such additional steps are costly and normally should be avoided.

Taking into account the foregoing factors, I have found that the amount of solubilizers required in preparing compositions in the lower portions of the processing temperature range may be as little as about 8% to about 30%, and preferably from about 10% to about 20% by weight of the charge materials.

Where volatilization of process materials is not of concern, and absorption capacity of wood to be treated is high, compositions having relatively low boric acid contents in the aqueous treating solutions can be made by carrying out the process at temperatures upwardly of about 50°C., without the use of boric acid solubilizers. Use of a solubilizer also can be omitted under certain, limited conditions, for example where high boric acid concentrations are not needed, or where limited absorption capacity of a particular wood product precludes impregnation of large amounts of fire retardant, or where the corresponding boric acid concentration of the treating solution is sufficiently low to avoid precipitation under ambient storage and handling temperatures, or where the practical and economic effects of either reheating to resolubilize precipitated solute, or of storing and handling of the solution at elevated temperatures to prevent precipitation may be feasible.

The quantity of synergist(s) will depend upon the degree of fire retardancy required and the particular synergist(s), or combined solubilizer/synergist(s) which are selected. The required amount of such materials generally may range from about 25 to about 40%, preferably from 30 to 38% by weight of the (non-aqueous) charge materials, except that urea is restricted in maximum amount to about 15 to 17% in order to limit undesirable hygroscopicity of the compositions. Amounts of urea up to such maximum limit are useful, not only to aid in solubilization of boric acid, but also (by virtue of its strong hygroscopicity) to serve to keep treated wood products from completely drying out by retaining a small amount of water in the products.

Where the fire retardant composition contains a component which acts both as a solubilizer and as a synergist, such multiple functions must be considered in determining the total amounts of such components and other solubilizers and synergists required to obtain a desired degree of fire retardancy. In such cases, the total amount of such materials together with non-solubilizing synergist(s) may range, for example, from about 15% to about 35%, and preferably from about 20% to about 30% of the weight of the charge materials.

In one embodiment of the invention, water, boric acid, dicyandiamide (synergist) and urea (serving as a combined solubilizer and controlled water retention agent), within weight ranges of each functional compound type as above described, are heated with agitation at a temperature between 30°C and 60°C, preferably at about 45°C. When maximum solution of boric acid is achieved, monoethanolamine (solubilizer) is added followed by ammonium hydroxide (solubilizer). When all components are dissolved, the solution is cooled to room temperature. The respective proportions of charge materials required, within the ranges of each material, in preparing this and other compositions in accordance with this invention readily can be determined experimentally in light of the principles and examples herein taught and provided.

Boric acid is an effective biocide. However, additional biocides and other materials may be added to the compositions of the invention, but such additives should not materially affect the non-resinous, non-hygroscopic and low acidity nature of the compositions or their fire retardant properties, and should not contribute other undesirable characteristics, such as production of noxious fumes, afterglow, etc. on high temperature exposure of the treated wood products.

Aqueous solutions of the fire retardant compositions of this invention can be used to treat wood products by any one of the various techniques which are well known in the art. Examples of such methods include dipping, soaking and vacuum or vacuum-pressure impregnation. The particular technique used will be determined by such factors as the species of wood being

treated, the thickness of the wood product, the degree of fire retardancy required and the intended end use of the treated wood product. The treating method and conditions to be employed also are factors to be considered in determining the solute composition and component concentrations of the aqueous treating solution.

After treatment of a wood product, it thereafter may be dried in a conventional manner at ambient temperature. Alternatively, drying may be accelerated by heating the product, for example, in a kiln to a temperature of from about 40°C to about 65°C, for a time sufficient to reduce the wood moisture content to about 10 to 20 percent, normally around 10%. Because the fire retardant compositions of the invention are essentially non-resinous, an extended, high temperature (e.g. 65°C or greater) curing cycle is not required. Therefore, wood strength is not impaired.

The following further examples will illustrate the invention.

#### Example 1

A 12.5% aqueous treating solution is prepared from 61.84 gm. (1 mole) boric acid, 11.22 gm. (0.18 mole) monoethanolamine, 11.22 gm. ammonium hydroxide (3.25 gm. - 0.19 mole NH<sub>3</sub>), 18.02 gm. (0.30 mole) urea, 6.15 gm. (0.08 mole) dicyandiamide, and 669.39 gm. (37.1 moles) water. Half of the water is heated to 45°C and, while agitating, the boric acid, urea and dicyandiamide are added. When about maximum solubility is achieved, the ethanolamine and ammonium hydroxide are added and agitation is continued until all of the components are in solution. The remainder of the water is added and the solution is cooled to room temperature.

A composition in accordance with Example 1 was prepared in sufficient amount to accommodate the immersion therein and impregnation therewith of four ponderosa pine fire tube specimens having dimensions of 3/8 inch x 3/4 inch x 40 inches. The specimens were submersed in a treating cylinder designed for pressure impregnation and a vacuum of about 30 inches of Hg was applied for 30 minutes, followed by a pressure impregnation period of 3 hours at about 150 psi. The pressure

then was released and the specimens removed from the cylinder and allowed to air dry for one day and then oven dried at about 50°C until an equilibrium moisture content of about 5 to 10% was reached. Other compositions, identified as Examples 2, 3 and 4 in Table 1 below, were similarly prepared and used to similarly treat additional similar wood samples. The ammonia in the formulations of Examples 1-3 is volatile and is removed essentially completely from the wood during drying.

The thus-treated specimens, as well as similar untreated wood control samples, and similar samples treated only with boric acid, monoethanolamine or urea, were subjected to fire tube tests in accordance with the procedure of ASTM E69-50. According to this standard, fire tube weight loss under 30% is considered acceptable fire retardancy. The specimens were oven-dried and equilibrated to a moisture content of about 5% and placed in a metallic tube having vent holes. The bottom ends of the specimens were positioned a distance of one inch from the top of a burner and a calibrated flame then was applied to the bottom of the samples. The burner was adjusted to provide a flame height of 11 inches and a temperature at the top of the fire tube (in the absence of a sample) of 175°C to 180°C. The samples, were suspended over the flame for a period of 4 minutes. In case of the untreated samples and each of the samples treated with boric acid, monoethanolamine or urea, burning continued after the pilot flame was removed. In each case, the weight of the non-consumed portion of the sample was subtracted from the original weight to determine weight loss. Such data are given in Table 1 wherein formulation percentages are by weight of charge materials.

Table 1

Examples (Formulations in wt. percent)	Retention pcf <sup>a</sup>	% B	% P	% B+P	Fire Tube Wt. Loss %
A. Untreated	0	0	0	0	85
B. Monoethanolamine	5	0	0	0	90
C. Urea	5	0	0	0	88
D. $H_3BO_3$ only	4.0 2.7 1.6	2.50 1.68 1.00	0 0 0	2.50 1.68 1.00	65 68 70
E. DRICON <sup>b</sup> : 70% GUP <sup>c</sup> +30% $H_3BO_3$	5.5 4.6	1.03 0.86	2.13 1.78	3.16 2.64	21 28
1. 57.3 $H_3BO_3$ 10.4 Mono- ethanolamine 10.4 $NH_4OH$ (29% $NH_3$ ) 16.7 Urea 5.2 Dicyandiamide	7.1 5.8 5.0	2.83 2.32 2.00	0 0 0	2.83 2.32 2.00	21 25 27
2. 58.1 $H_3BO_3$ 1.7 $NH_4OH$ (29% $NH_3$ ) 10.3 HMTA 11.5 Urea 5.7 Dicyandiamide 12.7 75% $H_3PO_4$	6.2 4.8	2.36 1.83	0.70 0.54	3.06 2.37	21 26
3. 50.0 $H_3BO_3$ 10.0 $NH_4OH$ (29% $NH_3$ ) 15.0 Urea 10.0 HMTA 15.0 GUP	5.9 5.0	2.05 1.73	0.54 0.46	2.59 2.19	20 25
4. 42.0 $H_3BO_3$ 41.1 $N_2B_4O_7 \cdot 10H_2O$ 8.5 Urea 8.4 Dicyandiamide	9.1 5.7	2.40 1.50	0 0	2.40 1.50	27 58

<sup>a</sup>pcf - pounds/cu. ft.<sup>b</sup>"DRICON" is a trademark of Hickson, Ltd.<sup>c</sup>GUP = guanylurea phosphate<sup>d</sup>HMTA = hexamethylenetetramine

The boron and phosphorus retentions of Table 1 are converted to boric acid [B(OH<sub>3</sub>)] and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) equivalents, by weight percent, in Table 2 wherein the ratios of weight percentages of those compounds as well as the similar ratios of elemental boron and phosphorus also are given.

Table 2

Example	Weight Percent		Weight Ratios	
	Boric Acid	Phosphoric Acid	Boric Acid/ Phosphoric Acid	B/P
D	14.3	0	-	-
	9.6	0	-	-
	9.1	0	-	-
E	5.9	6.7	0.88	0.48
	4.9	5.6	0.88	0.48
1	16.2	0	-	-
	13.3	0	-	-
	11.4	0	-	-
2	13.5	2.2	6.14	3.37
	10.5	1.7	6.18	3.39
3	11.7	1.7	6.88	3.80
	9.9	1.4	7.07	3.76
4	13.7	0	-	-
	8.6	0	-	-

From the data of Table 1, it can be seen that, used alone, neither monoethanolamine nor urea (Examples B and C) showed any significant fire retardant effect. Boric acid alone (Example D) had very little such effect, but, when present together with the other components of the Example 1 mixture, a drastic and unexpected synergistic effect is achieved. These data also include the results of preparation, treatment and fire tube testing, as above-described, of a similar wood sample (Example E) treated with a composition ("DRICON") in accordance with Oberley U.S. Patent No. 4,373,010. From such comparative data it is seen that the fire retardancy of the wood treated with the phosphorus-free

Example 1 composition is about equal to that of the sample treated with the high phosphorus, relatively highly acidic (about pH 3.5) DRICON composition. As above-described, compositions such as that used in Example 1 have the further advantage over acidic phosphorus-containing compositions such as that of Example E, of being nearly neutral (pH is in the range of about 6.5 to about 6.9) and hence free of harmful wood degradation by acid hydrolysis.

Examples 2 and 3 of Table 1 further illustrate the compositions of the invention. These compositions contain high percentages (respectively 58.1% and 50%) of boric acid together with other boric acid solubilizers (ammonia and hexamethylenetetramine) and supplemental solubilizers/synergists (phosphoric acid in Example 2 and guanylurea phosphate in Example 3 -- both of which compounds are limited to 15% or less in order to avoid high acidity of the compositions). Both Examples 2 and 3 show excellent fire retardancy. As in the case of Example 1, fire tube weight loss is in the range of 20 - 27%, as compared to a weight loss of 85% for untreated wood (Example A) and 65-70% for boric acid alone.

In Example 1 of Table 1, the amount of the monoethanolamine solubilizer is determined as a function of the minimum amount at which, in the presence of the synergists, urea and dicyandiamide, the desired amount of boric acid can be dissolved in water at the predetermined, practically low temperature, without the addition of so much monoethanolamine that unacceptable flame spreading would occur upon exposure to wood combustion temperatures. The amount of monoethanolamine required for such purpose can be reduced, and its contribution to flame spreading decreased, by using, in conjunction with the amine, a second solubilizer, such as ammonium hydroxide, which adds no fuel value to the composition. Similar considerations can easily be applied by those skilled in the art to select others of the described solubilizers and synergists and to balance the respective amounts of each in accordance with the principles of the invention as set forth herein.

For acceptable fire retardancy, an amount of fire retardant material, sufficient to exert effective fire retardancy on burning of a wood article, must be impregnated into and retained within the wood. On the other hand, with too large a quantity of fire retardant, impregnated wood product will become embrittled and of such increased density as to necessitate redesign for the intended application. In view of this latter factor, retained fire retardant materials should be kept under an amount which would significantly embrittle the wood product. The amount of fire retardant material needed to achieve acceptable fire retardancy is dependent upon factors such as wood species and density, and conditions of manufacturing a wood article, such as plywood. For example, such retention using an efficient fire retardant varies from as little as 2.5-3.0 pounds per cubic foot for Douglas fir lumber to retentions as high as 6 pounds per cubic foot for Southern yellow pine plywood. For effective fire retardance, the amount of effective fire retardant should be slightly greater than the threshold level determined to provide such adequate fire retardancy. Thus, from Examples 2-3 of Table 1, it will be seen that, with use of the compositions of this invention, adequate fire retardancy (below 30% fire tube weight loss) is achieved at retentions less than 6 pounds per cubic foot of the ponderosa pine samples. This result is obtained with concentrations of retained boron in the range of 2% or less. Further, such results are obtained with only very little phosphorus (0.46% to 0.70% as in Examples 2 and 3) or no phosphorus (Example 1) with a fire retardance equivalent to that of the most effective prior art compositions represented by Example E, containing about the same amount of retained fire retardant (4.6 pounds per cubic foot) and over 1% of phosphorus.

As also shown in Table 2, the best and nearest comparable prior art fire retardant composition ("DRICON"), Example E, has a B:P weight ratio less than 0.5:1, whereas the compositions of the invention as shown in Table 1 have a B:P weight ratio over 3:1, i.e. over 6 times greater. Similarly, on the basis of weight percent of retained fire retardant, in

terms of equivalent boric acid and phosphoric acid, the boric acid/phosphoric acid ratio, for the phosphoric acid-containing Examples 2 and 3, is about 7-8 times greater than that for Example E.

Example 4 of Table 1 contains borax as well as boric acid. At an acceptable level of retained fire retardant (for example, 5.7 pounds per cubic foot as shown for the second test composition of Example 4), the fire retardancy of such compositions is much less (58% fire tube weight loss) than the preferred compositions of this invention. This latter test illustrates the disadvantage of the use of metal salts such as borax in fire retardant compositions due to the action of such salts in reducing their effectiveness by deactivating boric acid as a fire retardant, on a mol-for-mol basis. While a sodium-containing formulation such as that of Example 4 can provide reasonable fire retardancy and satisfactorily low hygroscopicity and acidity, fire retardancy equal to that of the preferred compositions of this invention is possible only if the amount of fire retardant is increased to a level at which the impregnated wood becomes unacceptably dense and brittle -- as shown in the first of the two test compositions of Example 4. Although fire retardant performance of such compositions can be improved by increasing the amount of dicyandiamide and/or urea, higher than optimum retentions still are required.

In addition to the described technical advantages of the compositions of this invention as compared to "DRICON" type fire retardants, the new compositions also are substantially less costly than the "DRICON" compositions.

What is claimed is:

1. An improved, water soluble fire retardant composition adapted, in a water solution thereof, for impregnation of solid wood products and other cellulosic materials and comprising, by weight percent of the composition charge materials, excluding water solvent, from about 40% to about 70% of boric acid, at least one nitrogen-containing synergist material which is soluble in water at a solution temperature of from over 0°C. to under 100°C. in an amount which, in combination with boric acid, is effective to enhance the fire retardancy of wood products impregnated therewith as compared to that of the synergist material and boric acid alone, and a combined total of not more than about 15% of materials having an acid strength greater than boric acid, such composition, when introduced into wood products, having substantially no effect on hydrolysis of the wood cellulose and corrosion of metals in contact with the wood product.
2. A composition according to claim 1 additionally containing at least one solubilizer which is water soluble in an amount effective to increase water solubility of boric acid in the presence of the synergist material at a temperature within the aforesaid solution temperature range.
3. A composition according to claim 2 wherein the composition is essentially free of materials having an acid strength greater than that of boric acid.
4. A composition according to claim 2 wherein the solution temperature is in the range from about 20°C. to about 65°C. and the composition contains at least about 45% boric acid, is substantially non-resinous and free of alkali metals and alkaline earth metals, and is capable of being dried, after impregnation of an aqueous solution thereof into a wood product, at a temperature under about 65°C.

5. A composition according to claim 4 wherein the boric acid content is from about 50% to about 65%.

6. A composition according to claim 4 wherein the boric acid content is from about 50% to about 60%.

7. A composition according to claim 4 wherein the synergist material is selected from the group consisting of semicarbazide, guanidine, cyanamide, dicyandiamide, urea, guanylurea, guanylurea phosphate, monoammonium phosphate and diammonium phosphate, and mixtures thereof, and wherein urea is limited to a maximum amount of about 17% and guanylurea phosphate, monoammonium phosphate and diammonium phosphate are limited in combined amount to less than 20%.

8. A composition according to claim 7 wherein the group of synergist materials additionally includes melamine, biuret and oxamide and mixtures thereof with each other and with other synergists of the group and wherein, when the composition contains such an additional synergist, the composition also contains an amount of a supplemental solubilizer in amount sufficient to dissolve an effective amount of such additional synergist in the water solution.

9. A composition according to claim 8 wherein the amount of urea and the combined amount of the phosphorus-containing materials each is limited to about 15%.

10. A composition according to claim 9 wherein the additional synergist material is melamine and the supplemental solubilizer is formaldehyde.

11. A composition according to claim 7 wherein the solubilizer material is selected from the group consisting of ammonia, basic nitrogen compounds other than ammonia, monohydric alcohols, polyols, and mixtures thereof with or without ammonia.

12. A composition according to claim 11 wherein the basic nitrogen compounds other than ammonia are selected from the group consisting of ammonium carbonate, strongly basic amines having a  $pK_B$  under about 5, and more weakly basic compounds having a  $pK_B$  of about 5 or larger.

13. A composition according to claim 12 wherein the basic amines are more strongly basic than ammonia.

14. A composition according to claim 13 wherein the basic amines are selected from the group consisting of primary, secondary and tertiary alkylamines and alkanolamines, and hexamethylenetetramine.

15. A composition according to claim 14 wherein the alkylamines and alkanolamines are selected from the group consisting of ethylamines, propylamines, ethanolamines and propanolamines, and the weakly basic compounds are selected from the group consisting of formaldehyde-amine addition compounds, hydrazine, ammonium carbonates and ammonium carbamate, the monohydric alcohol is a saturated alcohol selected from the group consisting of methanol, ethanol, N-propanol, isopropanol, and butyl and amyl alcohols, and the polyol is selected from the group consisting of dihydric alcohols, trihydric alcohols, higher polyhydric alcohols, monosaccharides and disaccharides.

16. A composition according to claim 15 wherein the saturated monohydric alcohol is methanol, the dihydric alcohol is selected from the group consisting of ethylene glycol and propylene glycol, the trihydric alcohol is glycerol, the higher polyhydric alcohol is selected from the group consisting of mannitol and sorbitol, the monosaccharide is selected from the group consisting of glucose and fructose, and the disaccharide is sucrose.

17. A composition according to claim 9 comprising from an effective amount up to about 25% by weight of a boric acid solubilizer selected from the group consisting of monoethanolamine, hexamethylenetetramine, ammonia, phosphoric acid and guanylurea phosphate, wherein ammonia, phosphoric acid and guanylurea phosphate each is limited in maximum amount to about 15% and the combined amount of phosphoric acid and guanylurea phosphate is limited to about 15%.

18. A composition according to claim 17 wherein the synergist material comprises from an effective amount up to about 10% by weight of dicyandiamide, and from an effective amount up to about 17% by weight of urea as a combined synergist and for retaining a minimum required amount of moisture in a wood product impregnated with a water solution of such composition.

19. A composition according to one of claims 2 and 4 wherein the synergist material is selected from the group consisting of semicarbazide, guanidine, cyanamide, dicyandiamide, urea, guanylurea, guanylurea phosphate, monoammonium phosphate and diammonium phosphate, and mixtures thereof, the solubilizer material is selected from the group consisting of ammonia, basic nitrogen compounds other than ammonia, monohydric alcohols, polyols, and mixtures thereof with or without ammonia, urea is limited to a maximum amount of about 17%, and guanylurea phosphate, monoammonium phosphate and diammonium phosphate are limited in combined amount to less than 20%.

20. A solution for treating solid wood and other cellulosic products to improve the fire resistance thereof, comprising an aqueous solvent and a solute having a composition according to one of claims 1, 2, 3, 4 and 11.

21. A solution concentrate adapted for dilution with water to form a treating solution for solid wood and other cellulosic products to improve the fire resistance thereof, comprising an aqueous solvent and a solute having a composition according to one of claims 1, 2, 3, 4 and 11 and wherein the boric acid comprises from over 10% to about 20% by weight of the solution.

22. A solution for treating solid wood and other cellulosic products to improve the fire resistance thereof, comprising an aqueous solvent and a solute having a composition according to one of claims 1, 2, 3, 4 and 11 and wherein the boric acid comprises from about 5% to about 15% by weight of the solution.

23. A wood product impregnated with an aqueous solution of a fire retardant composition according to one of claims 1, 2, 3, 4 and 11.

24. A wood product impregnated with an aqueous solution of a fire retardant composition according to one of claims 1, 2, 3, 4 and 11 and dried after impregnation and containing up to about 6 pounds per cubic foot of retained fire retardant, wherein the weight ratio of retained boron to phosphorus is at least 3 to 1.

25. A wood product impregnated with an aqueous solution of a fire retardant composition according to one of claims 1, 2, 3, 4 and 11 and dried after impregnation and containing up to about 6 pounds per cubic foot of retained fire retardant, wherein the weight ratio of retained boron to phosphorus is at least 3 to 1 and the product contains, by weight percent, at least about 1.5% of retained boron and from substantially none to less than about 0.75% phosphorus.

26. A method of treating a cellulosic product to impart fire retardancy thereto comprising impregnating said article with a fire retardant amount of a composition according to one of claims 1, 2, 3, 4 and 11.

27. A process for forming a treating solution for imparting fire retardance to wood and other cellulosic products comprising forming an initial aqueous solution containing from about 15% to about 20% by weight of boric acid by adding to water, within a reaction temperature range from about 20°C to about 65°C, boric acid and at least one non-acidic boric acid solubilizer which is soluble under such conditions in an amount effective to provide such minimum boric acid content, and at least one synergist material which is soluble under such conditions in an amount effective to provide, with boric acid, a fire retardancy greater than that of boric acid or the synergist material alone, agitating the solution until the reactants are substantially fully dissolved, cooling and diluting the solution to a boric acid concentration in the range from about 5% to under 15% by weight of the diluted solution.

28. A process according to claim 27 wherein the reaction temperature range is from about 30°C. to about 45°C.

29. A process according to one of claims 27 and 28 wherein the solute comprises, by weight percent, from about 50% to about 70% boric acid, from about 8% to about 30% of solubilizer, and from about 15% to about 35% of synergist material.

30. A process for making a treating solution for imparting fire retardance to wood and other cellulosic products comprising adding to water boric acid and at least one synergist material and agitating the solution at a reaction temperature in the range from about 50°C to under 100°C, and wherein the boric acid addition is in an amount from about 5% to about 12% by weight of solution and the

synergist material addition is in an amount which is soluble at the reaction temperature in an amount at least sufficient to provide, with the boric acid, a fire retardance greater than that of boric acid or the synergist material alone, continuing agitation of the solution until the additions are substantially completely dissolved, and cooling the solution to ambient temperature.

31. A composition according to one of claims 1, 2, 4 and 11 wherein the mol ratio of nitrogen to boron or to boron plus phosphorus is from about 0.5:1 to about 2:1.

32. A composition according to one of claims 1, 2, 4 and 11 wherein the mol ratio of nitrogen to boron or to boron plus phosphorus is from about 0.8:1 to about 1.5:1.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/03700

## II. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>3</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

INT CL(5): C09K 21/02  
U.S CL.: 252/607

## II. FIELDS SEARCHED

Classification System	Minimum Documentation Searched <sup>4</sup>	
	Classification Symbols	
USA	252/607, 601, 609	428/921
	106/18.16, 18.17	
	427/421, 439,440	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>14</sup>

Category <sup>6</sup>	Citation of Document, <sup>10</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X/Y	US, A, 4,373,010 Published 08 February 1983 (OBERLEY) columns 2-4	1-32/1-32
X/Y	US, A, 4,725,382 Published 16 February 1988 (LEWCHALERMNONG) column 3-4, and column 7.	1-32/1-32
Y	US, A, 4,461,721 Published 24 July 1984 (GOETTSCHE ET AL) column 1 lines 1-64	1-32
Y	US, A, 4,076,540 Published 28 February 1978 (STOSSEL) column 7, lines 23-68, column 12 lines 37-59	1-32
A	US, A, 3,811,992 Published 21 May 1974 (HANDA) abstract, column 4 lines 42-75	1-3,23-25
Y	US, A, 3,874,990 Published 01 April 1975 (SURDYK) column 2-4	1-3,23-25

### \* Special categories of cited documents: <sup>15</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search <sup>9</sup>

14 SEPTEMBER 1990

International Searching Authority <sup>1</sup>

ISA/US

Date of Mailing of this International Search Report <sup>10</sup>

07 NOV 1990

Signature of Authorized Officer: <sup>11</sup> ROBERT L. STOLL <sup>12</sup> Nguyn

INTERNATIONAL DIVISION